

Design and Synthesis of Novel Block Copolymers for Efficient Opto-Electronic Applications

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ABSTRACT

It has been predicted that nano-phase separated block copolymer systems containing electron rich donor blocks and electron deficient acceptor blocks may facilitate the charge carrier separation and migration in organic photovoltaic devices due to improved morphology in comparison to polymer blend system. This paper presents preliminary data describing the design and synthesis of a novel Donor-Bridge-Acceptor (D-B-A) block copolymer system for potential high efficient organic opto-electronic applications. Specifically, the donor block contains an electron donating alkyloxy derivatized polyphenylenevinylene (PPV), the acceptor block contains an electron withdrawing alkyl-sulfone derivatized polyphenylenevinylene (PPV), and the bridge block contains an electronically neutral non-conjugated aliphatic hydrocarbon chain. The key synthetic strategy includes the synthesis of each individual block first, then couple the blocks together. While the donor block stabilizes and facilitates the transport of the holes, the acceptor block stabilizes and facilitates the transport of the electrons, the bridge block is designed to hinder the probability of electron-hole recombination. Thus, improved charge separation and stability are expected with this system. In addition, charge migration toward electrodes may also be facilitated due to the potential nano-phase separated and highly ordered block copolymer ultra-structure.

Keywords: Opto-electronic materials, photovoltaic materials, plastic solar cells and photo detectors, block copolymers, nano-phase separated structures.

1. INTRODUCTION

The technique of converting solar energy into electrical power by means of photovoltaic materials has been widely used in spacecraft power supply systems, and is more and more extended for terrestrial applications to supply autonomous customers (portable apparatus, houses, automatic meteorostations, etc.) with electric power.¹ Sunlight is free, it does not use up an irreplaceable resource, and its conversion to electricity is non-polluting. However, one major challenge of the large-scale application of this technique is the low energy density of sunlight. To generate appreciable electrical power in space and on the earth, it is necessary to collect sunlight from large areas. If the current commercially available inorganic semiconductor solar cells are used, the cost of electricity obtained in such a way would exceed substantially that generated by conventional methods, and this is one reason retarding the development of large-scale solar power industry. Organic and polymeric photovoltaic cells, with their versatile fabrication schemes and low cost on large-scale production, exhibit potential for future large-scale solar industry. For space and any portable applications, lightweight and flexible shape of polymers is a key advantage. While the power conversion efficiency for inorganic photovoltaic cells have reached over 20%,¹ it is still less than 7% for the recently developed polymer photovoltaic systems.²⁻⁵ Therefore, development of highly efficient polymeric photovoltaic materials, and to better understand the fundamental mechanisms involved in polymer opto-electronic processes has become a critical research effort.

The development of π -electron conjugated polymers, and the ability to dope these polymers over a wide range from insulator to conductor, has resulted in the creation of a new class of materials that combines the electronic and optical properties of inorganic semiconductors and metal conductors with the attractive mechanical and processing advantages of polymers.⁶⁻⁷ The extended π -orbitals and often a specific packing order of these conjugated polymers results in unique multi-dimensional electronic structures.⁸⁻⁹ Most of the electronic and photonic phenomena known in conventional inorganic

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semiconductors have also been observed in these conjugated polymers. Most semi-conducting conjugated polymers appear to have a band gap that lies in the range 1.5–3 eV, which makes them ideally suited as opto-electronic devices working in the optical light range.²⁻⁵ Electronic materials derived from conjugated polymers have been studied or developed for diverse items such as sensors, light-emitting diodes, actuators, field effect transistors, corrosion protection agents, battery components, photovoltaic cells, etc.^{6-7, 10-12}

Photo-induced charge generation and separation observed in polymer composites of donors (electron-rich organic species, such as alkyloxy derivatized PPV or polythiophenes PThs) and acceptors (electron-deficient organic species, such as C₆₀, CN-PPV, or other acceptor groups) provided a potential molecular approach to high efficiency opto-electronic conversion.^{2-5, 10-18} Since the time scale for photo-induced exciton (electron-hole pairs and related species) generation in organic systems is in sub-pico or nano seconds, at least a thousand times faster than the radiative or non-radiative decay of the excitons,¹⁸⁻¹⁹ the quantum efficiency for exciton generation is near unity. Since the donor (D) helps stabilizing and transporting the positive charge (holes), and acceptor (A) helps stabilizing and transporting the negative charge (electrons), the photo-induced charge separation facilitated by the donor and acceptor interfaces offer great potential for more efficient opto-electronic applications. Such polymeric systems have been demonstrated using PThs/CN-PPV bilayers,³ MEH-PPV/CN-PPV blends,¹³⁻¹⁴ MEH-PPV/C₆₀ bilayers and blends,^{4, 11} PThs/C₆₀ blends,¹⁵ MEH-PPV/PS-C₆₀ di-block copolymers,¹⁷ etc., as active materials.

Although the quantum efficiency of photo-induced exciton generation is near unity, the overall polymer photovoltaic device power conversion efficiency is limited by at least three key factors: 1) How convenient the excitons can migrate or diffuse to donor or acceptor interfaces; 2) How easy the charge would recombine (including exciton decay); 3) the charge carrier mobility to the electrodes.^{11, 18} Therefore, the ideal material should be a continuous interpenetrating network of donor-bridge-acceptor nano-phases that possessing large or convenient donor and acceptor interfacial areas to facilitate photo-induced charge (electron and hole) separation, to minimize the probability of charge recombination, and to create a continuous and smooth transporting passageways for separated charges to move easily to the electrodes. In fact it has been demonstrated that much higher (e.g., two orders of magnitude) opto-electronic energy conversion efficiencies were obtained with devices using D/A blends (also called “bulk D/A heterojunction” materials) than devices with D/A bilayers or the pristine donor or acceptor polymers, and this was attributed mainly to the increased interfacial area in D/A blend systems.¹⁰⁻¹⁶ However, it is not easy to obtain a uniform, ordered nano-phase separation simply by blending donor and acceptor polymers. The very low charge carrier collection efficiencies in polymeric blend systems are believed mostly due to poor phase separation (inhomogeneous too small or too large scale phase separation) that cause poor charge separation at interfaces and poor charge mobility in the materials.

Block copolymer phase behavior has been studied for several decades. Nevertheless, recent experimental and theoretical studies revealed that our understanding of block copolymer system is far from clear. Even the simplest di-blocks of some common polymers continue to yield surprising complexity.²⁰⁻²¹ Block copolymer melts exhibit behavior remarkably similar to conventional amphiphilic systems such as lipid-water mixtures, soap, and surfactant solutions. The incompatibility between the blocks leads to the formation of unique micro- or nano- phase separated and ordered structures. The connection between distinct blocks imposes severe constraints on possible equilibrium states, this results nano-domain structures such as lamellae (LAM), hexagonally packed rods (HEX), spheres packed on a body-centered cubic lattice (BCC), hexagonally perforated layers (HPL) and at least two bi-continuous phases: the ordered bi-continuous double diamond phase (OBDD) and the gyroid phase. The morphology of block copolymers is affected by chemical composition, size of each block, temperature and other factors.²²

Block copolymer approach to opto-electronic material provides some intrinsic advantages that could hardly be achieved in polymer composite blend systems. Recent study of MEH-PPV/Polystyrene-C₆₀ (D-A) di-block copolymers demonstrated a nice honeycomb shaped nano phase separated structures.¹⁷ In our system, by building an electron rich donor block, an electron neutral bridge block, and an electron deficient acceptor block into D-B-A type block copolymer, one could actually maximize charge separation and minimize charge recombination at the same time. The charge separation is maximized because there are larger and more uniform interfacial areas in the nano-phase separated donor and the acceptor blocks or phases. Furthermore, the interfacial area can be conveniently adjusted via block copolymer segment size control. Every donor block can be built in a convenient reach of an acceptor block within the exciton diffusion range (typically less than 20 nm).^{2, 15} Therefore, one limitation to the efficient charge separation (due to long range exciton diffusion) is reduced.¹⁴ Since the probability for the donor and acceptor π -orbitals to directly overlap is greatly reduced due to the introduction of a non conjugated bridge block, the charge recombination between the donor and acceptor blocks is also significantly

retarded.²³⁻²⁴ On the other hand, through smart molecular design, one may introduce driving force to induce the identical blocks to form a unique π -stacked ordered structure. Such oriented and stacked π -systems have been reported to have significantly enhanced charge mobility.^{9, 25-26} Though a non conjugated bridge is used, overall charge mobility will not be affected significantly since intra-molecular charge migration and exciton diffusion can also proceed effectively through σ -bonds or through space.²³⁻²⁸

2. EXPERIMENTAL AND RESULTS

1. Materials and instruments

All starting materials, reagents and solvents were purchased from commercial sources and used directly except noted otherwise. NMR data were obtained using a Bruker Avance 300 MHz spectrometer. Elemental analysis was done on a Perkin-Elmer PE2400 II Analyzer. FT-IR Spectra were collected on either a Nicolet Avatar FT-IR or a Bruker IFS66 FT-IR spectrophotometer using 16 scans for each spectrum with background correction. Perkin-Elmer TMA-7/DSC-6/TGA-6 systems were used to characterize the thermal property of the materials. Molecular weight analysis of polymers was done using a Viscotek T60A/LR40 triple-detector GPC system with mobile phase of THF at ambient temperature (Universal calibration based on polystyrene standards is used). UV-VIS spectra were collected using a Varian Gary-5 spectrophotometer. Optic luminescence spectra were obtained from an ISA Fluoromax-3 spectrofluorometer.

2. Donor Block Synthesis (Figure 1)

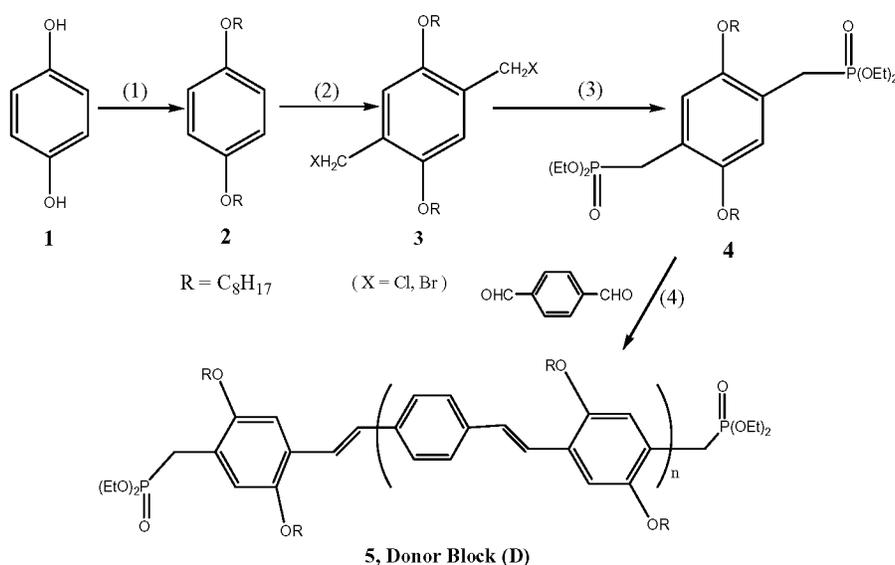


Figure 1. Synthetic scheme of a donor (D) block.

1, 4-bis(2-ethyl-hexyloxy)-benzene (2): 100 mmol (11.0 g) of hydroquinone **1** and 200 mmol of KOH were mixed in 120 ml acetonitrile, stirred at 60°C for 30 minutes. Then 200 mmol of 2-ethylhexyl bromide were added to the reaction mixture in 30 minutes. The reaction was stirred at 60°C for 16 hours and then cooled to room temperature. Add about 60 ml chloroform and about 200 ml water to the reaction mixture, collect the organic phase and wash with water three times to remove inorganic impurities. After dried with magnesium sulfate, and the solvent was removed, 31.7g (95% yield) brown viscous liquid **2** was obtained. ¹H NMR (CDCl₃) δ (ppm): 6.85 (s, 4H, phenyl), 3.75(d, 4H, -OCH₂), 1.75 (m, 2H, 3°H), 1.29 (m, 16H, methylene), 0.96 (m, 12H, -CH₃).

2,5-bis(bromomethyl)-1,4-bis(2-ethyl-hexyloxy)-benzene (3): To a mixture of **2** (16.7 g, 50 mmol), paraformaldehyde (1.54 g, 100 mmol), and 80 ml glacial acetic acid, 10 ml of a 31 wt% HBr/acetic acid solution was added rapidly. The mixture was stirred and kept at 85°C for 12 hours and then poured into 150 ml water. After 60 ml of chloroform was added, the organic phase was collected and washed with water three times, dried with MgSO₄. After solvent was removed, 20.36g

(95% yield) thick brown liquid **3** was obtained. $^1\text{H NMR}$ (CDCl_3) δ (ppm): 6.85 (s, 2H, phenyl), 4.56 (s, 4H, $-\text{CH}_2\text{Br}$), 3.85 (d, 4H, $-\text{OCH}_2$), 1.75 (m, 2H, 3°H), 1.29 (m, 16H, methylene), 0.96 (m, 12H, $-\text{CH}_3$).

[2,5-bis-(2-ethyl-hexyloxy)-benzyl] 1,4-diphosphoric acid diethyl ester (4): 8.55g (10 mmol) of **3** and 3.3g (20 mmol) $\text{P}(\text{OEt})_3$ were mixed in 120 ml anhydrous dioxane and refluxing for two days. After dried with potassium carbonate and the solvent was removed, 9.2g (95% yield) thick, oil-like brown liquid **4** was obtained. $^1\text{H NMR}$ (CDCl_3) δ (ppm): 6.92 (s, 2H, phenyl), 4.05(d, 4H, $-\text{OCH}_2$), 3.75 (m, 8H, -phosphonic methylene), 3.23 (m, 4H, $-\text{CH}_2\text{P}$), 1.75 (m, 2H, 3°H), 1.29 (m, 28H, methylene), 0.96 (m, 12H, $-\text{CH}_3$). (Note: In this reaction, very dry dioxane should be used, a moisture contaminated dioxane may not work well.)

Donor block (D, 5): In a 100 ml three-necked flask, 0.64 g (1.0 mmol) of diphosphate monomer **4**, 0.13g (1.0 mmol) of Benzene-1,4-dicarbaldehyde and 2.0 g of $t\text{-BuOK}$ were dissolved in 20 ml dry THF. The mixture is stirred as vigorously as possible. The reaction time and temperature are varied in order to get different molecular weight (see Table 1). The reaction can be quenched by adding little extra amount of diphosphate monomer **4**. The product mixture is then transferred to a 100 ml separating funnel. Dichloromethane and water (20 ml each) are used to rinse the flask. The funnel was shaken thoroughly and the organic phase collected. The aqueous layer is extracted with 5 ml of dichloromethane and the extracted portion was combined with organic phase. After drying and solvent removal of the organic phase, a bright brown luminescent semi-solid polymer is obtained. $^1\text{H NMR}$ (in CD_2Cl_2) analysis shows the aldehyde protons of monomers disappeared completely and that new double bond alkene protons were shown at around 7.6-7.3 ppm. Molecular weight analysis results by GPC are listed in Table 1 below.

Reaction ID	Reaction Condition	Mw (Dalton, via GPC)	Average # of repeat units	Average size (nm)
1	70°C for 24 hours	10800	24	29
2	70°C for 6 hours then room temperature for 12 hours	8600	19	23
3	70°C for 4 hours then room temperature for 8 hours	3800	8	10

Table 1 Donor Block Size versus Synthetic Condition

3. Acceptor block synthesis (Figure 2)

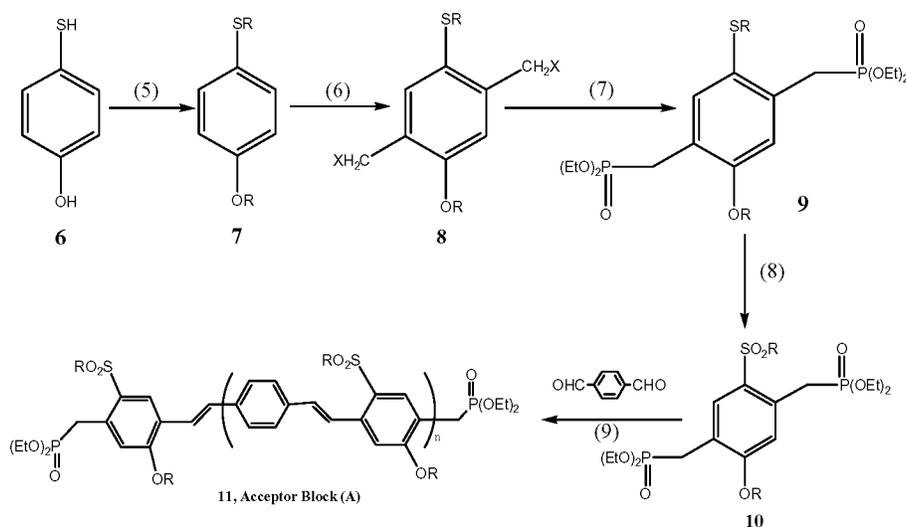


Figure 2. Synthetic scheme of an acceptor (A) block.

1-(2-ethyl-hexyloxy)- 4-(2-ethyl- hexylsulfide) benzene (7): 10g (71.3 mmol) of 4-mercaptophenol **6** and 39.3g (285 mmol) K_2CO_3 were mixed in 240 ml CH_3CN . After 10 minutes stirring, 55 ml 2-ethylhexyl bromide (285 mmol) was added. The reaction solution was heated up to 80°C and kept at this temperature for 24 hours. After the reaction was stopped and cooled to room temperature, the product mixture was added 200 ml chloroform and washed four times with water to remove inorganic impurities. The organic phase was dried over $MgSO_4$, and solvent was removed by a rotary evaporator. The residue was further purified by vacuum distillation. 22.5g brown liquid **7** was obtained (yield: 90%). 1H NMR ($CDCl_3$) δ (ppm): 7.80 (d, 2H, phenyl), 7.00 (d, 2H, phenyl), 3.90 (d, 2H, $-OCH_2$), 2.95 (d, 2H, $-SCH_2$), 1.85 (m, 2H, 3°H), 1.40-1.20 (m, 16H, methylene), 0.95 (m, 12H, $-CH_3$).

[2-(2-ethylhexyloxy)-5-(2-ethyl-hexylsulfide)]-1,4-bis-(chloromethyl)-benzene (8): 3.5g (10 mmol) of **7**, 1.54g (50 mmol) paraformaldehyde (CH_2O)_n, 100 ml HCl (1M in acetic acid), and 4 ml water were mixed. The mixture was stirred and heated up to 90°C, and keep the reaction at 90°C for 48 hours. After the reaction was stopped, the product mixture was poured into 10% Na_2CO_3 ice water solution, extracted by 20ml chloroform 3 times. The organic phase was collected and washed with water 3 times, dried over $MgSO_4$, and solvent was removed by a rotary evaporator. 3.83g of **8** was obtained (yield: 85%). 1H NMR ($CDCl_3$) δ (ppm): 7.30 (s, 1H, phenyl), 6.90(s, 1H, phenyl), 4.65(s, 2H, $-CH_2Cl$), 4.50(s, 2H, $-CH_2Cl$), 3.80(d, 2H, $-OCH_2$), 2.80(d, 2H, $-SCH_2$), 1.85 (m, 2H, 3°H), 1.40-1.20 (m, 16H, methylene), 0.95 (m, 12H, $-CH_3$).

[2-(2-ethylhexyloxy)-5-(2-ethylhexylsulfide)]-1,4-bisbenzyl-phosphonic acid diethyl ester (9): 3.83g of **8** (8.5 mmol) and 3.154g liquid $P(OEt)_3$ (19 mmol) were mixed together directly without any solvent, raise the temperature to 150°C and stir under inert gas for 24 hour. After purification via vacuum distillation, 5.5g of **9** was obtained (yield: 100%). 1H NMR ($CDCl_3$) δ (ppm): 7.50 (s, 1H, phenyl), 6.95 (s, 1H, phenyl), 3.90-3.50 (m, 10H, $-OCH_2-$, $-P(O)(OCH_2R)_2$), 3.15 (d, 4H, *ph*- $CH_2-P(O)(OR)_2$), 2.85 (d, 2H, $-SCH_2$), 1.85 (m, 2H, 3°H), 1.50-1.00 (m, 28H, methylene), 0.95 (m, 12H, $-CH_3$).

[2-(2-ethylhexyloxy)-5-(2-ethylhexylsulfone)]-1,4-bis-benzyl-phosphonic acid diethyl ester (10): 5.5g (8.5 mmol) of **9** and 30ml glacial acetic acid was heated up to 116-120°C, then 1.7g H_2O_2 (30% in water) was added in 4 times (10 mins each time), keep at above temperature and stirring for another 3 hours. After reaction was stopped and the temperature was cooled to room temperature, the product mixture was poured into water and organic product was extracted with 30ml chloroform 2 times. After solvent removal, a tan oil was obtained and added to a 30ml ethanol solution ($C_2H_5OH:H_2O = 1:1$) (10% NaOH added), stirred overnight, extracted with ether, and dried by $MgSO_4$. After solvent was removed by a rotary evaporator, 5.4g of **10** were obtained (yield: 80%). 1H NMR ($CDCl_3$) δ (ppm): 7.70 (s, 1H, phenyl), 6.75 (s, 1H, phenyl), 3.90-3.50 (m, 12H, $-OCH_2-$, $-SO_2CH_2-$, $-P(O)(OCH_2R)_2$), 3.15 (d, 4H, *ph*- $CH_2-P(O)(OR)_2$), 1.85 (m, 2H, 3°H), 1.50-1.00 (m, 28H, methylene), 0.95 (m, 12H, $-CH_3$).

Acceptor block (A, 11): 0.24g (1.8 mmol) of 1, 4-benzene dialdehyde and 1.3g **10** (2 mmol) (mole ratio of 1,4-benzene dialdehyde:**10** = 9:10) were dissolved in 50ml dry THF, and 0.44g (4 mmol) t-BuOK in 20ml dry THF was added drop wise under dry nitrogen atmosphere. The resulting reaction mixture was stirred for 24hrs at room temperature and subsequently poured into 400ml water. HCl (1M) was added to neutralize the aqueous phase until pH=7, and the aqueous phase were extracted with $CHCl_3$ (2 x 200mL). The combined organic phase were washed with water twice and dried over $MgSO_4$. After the removal of solvent, 0.96g polymer **11** was obtained as a dark brown luminescent high viscosity gel. GPC shows $M_w = 3,000$. 1H NMR δ : 8.20-7.90(m, phenyl-H), 7.70-7.50 (m, phenyl-H), 7.40(m, vinyl-H), 7.20-7.00(m, phenyl-H), 7.00-6.80(m, vinyl-H), 4.05-3.50(m, $-OCH_2-$, $-SO_2CH_2-$, $-P(O)(OCH_2R)_2$), 3.15(d, *ph*- $CH_2-P(O)(OR)_2$), 1.85 – 0.95 (m, $-CH_2-CH-(CH_2CH_3)(CH_2)3-CH_3$, $-P(O)(OCH_2CH_3)_2$). No aldehyde groups were found in polymer NMR spectrum. Since the estimated length for each repeat unit is about 1.2 nm, therefore, the average length of synthesized acceptor block **11** is about 6 nm (calculated based on $M_w=3000$, or approximately 5 repeat units).

4. Bridge block synthesis (Figure 3)

temperature may yield mono bromomethylation product. When converting the bromomethylene unit into the phosphoric acid diethyl ester in step (3), very dry dioxane should be used, otherwise the reaction may not proceed as expected.

In step (6) of attaching two $-\text{CH}_2\text{X}$ ($\text{X}=\text{Br}, \text{Cl}$) to the compound **7**, three different halomethylation reagents, including hydrogen bromide (32% in acetic acid), concentrated HCl water solution, and hydrogen chloride (1M in acetic acid) were examined, yet HCl (1M in acetic acid) was finally selected for several reasons. First, though HBr bromomethylation were very efficient in step (2) (more efficient than chloromethylation), it was not successful in step (6). This was probably due to HBr first oxidizes the electron donating sulfide (SR) unit into electron withdrawing sulfoxide (SOR) or sulfone (SO_2R) units that deactivate electrophilic bromomethylation reaction on aromatic ring. In contrary, HCl is not expected to oxidize sulfide unit easily. Second, with little amount of water in the reaction media, the reaction stops at di-chloromethylation substitution regardless the excess amount of $(\text{CH}_2\text{O})_n$. The time of completing di-chloromethylation is extended with increasing amount of water in reaction media, yet the side products are dramatically reduced at the same time.

When synthesizing donor block **5** in step (4) or acceptor block **11** in step (9), the average block sizes or lengths can be controlled via reaction conditions, such as reaction time, temperature or the monomer ratios. For equal molar coupling, the reaction can be quenched by adding extra amount of diphosphate monomer **4**. As shown in Table 1, the average block size (or average block length in nm) is generally proportional to the reaction time or temperature. Therefore, the polymer nano phase size can be conveniently controlled by the synthetic reaction control. This also demonstrates that traditional synthetic methods may be used for many potential nano structure materials fabrications. In our current system, the size of the bridge block can also be varied by using different length alkane dibromide **13** or related compounds. One of our ongoing and future research objectives is to investigate and reveal the correlation between materials bulk opto-electronic properties and the sizes or lengths of each block within the maximum charge diffusion length.

4. SUMMARY

Preliminary results on the design and synthesis of a novel Donor-Bridge-Acceptor (D-B-A) block copolymer system are presented. According to previous work, this approach and synthetic scheme may be useful for developing highly efficient organic opto-electronic materials. Specifically in our system, the donor block contains an electron donating alkyloxy derivatized polyphenylenevinylene (PPV), the acceptor block contains an electron withdrawing alkyl-sulfone derivatized polyphenylenevinylene (PPV), and the bridge block contains an electronically neutral non-conjugated aliphatic hydrocarbon chain. While the donor blocks help stabilizing and transporting the positive holes, the acceptor blocks help stabilizing and transporting the electrons, the bridge block is designed to retard the electron-hole recombination. Thus, improved charge separation and mobility are expected with this system. In addition, charge migration toward electrodes may also be facilitated due to the potential nano-phase separated and highly ordered block copolymer ultra-structure. The key synthetic strategy we developed includes the synthesis of finite and desired sized individual copolymer blocks first, then couple the blocks together. In this way, the size of the polymer nano phases can also be controlled. The molecular approach presented here may also be useful for fabricating other block copolymer nano structures.

5. ACKNOWLEDGEMENT

Supports from NASA (grant #NAG3-2289), DOE (CMR center grant) & NSF (CPMR center grant) are gratefully appreciated.

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